Studies on the Thiophene Analogues of Malachite Green. I.

Protolytic Equilibria and Reaction Rate Constants of

Thiophene Green in Aqueous Solutions

RUNE CIGÉN and GÖSTA BENGTSSON

*Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund,
Lund, Sweden*

The protolytic equilibria and the rate constants of a Thiophene
analogue of Malachite Green (MG), named Thiophene Green (TG),
have been investigated spectrophotometrically in aqueous solutions
with constant ionic strength 0.5 M at 20.0°C.

The results of the measurements have been compared with the
results of the corresponding measurements of MG and the hydroxy-
and methoxy-derivatives of MG. It was found that the hydration
reactions of TG proceed more slowly and that the values of the hydra-
tion constants K_2 and $1/K_6$ are lower in TG than in MG. In this respect
TG is similar to the *ortho*- and *para*-hydroxy and -methoxy derivatives
of MG.

The reaction scheme used in previous investigations of MG and
of derivatives of MG has been extended for the reactions in strongly
acid solutions in order to explain some results of the kinetic measure-
ments of TG.

The dyestuff Thiophene Green (TG) was first prepared by Levi[1]. Later Mason
and Nord[2,3] have investigated Thiophene Green and some derivatives of it
as regards their absorption curves, which were compared with the absorption
curve of Malachite Green.

Thiophene Green

The present investigation is devoted to the protolytic and hydration reac-
tions of TG in aqueous solutions, which have a constant ionic strength of 0.5 M.

The same reaction scheme that has been used in earlier studies on deriva-
tives of Malachite Green[4-7] has been tried on Thiophene Green. It was found

that in its reactions TG is similar to Malachite Green. However, the substitution of a phenyl group for a thienyl group has a marked influence on the hydration equilibria and the rate constants. Furthermore, the kinetic measurements in HCl + KCl-buffers indicate a more complicated reaction scheme than that which was used for Malachite Green. In the discussion part of this paper the differences between Malachite Green and Thiophene Green will be further treated.

In neutral aqueous solutions Thiophene Green is really green in contrast to Malachite Green and many of its derivatives, which are blue or blue-green. If the solution of TG is made acid, pH $\approx$ 0, it turns red immediately and is then partially decolourized owing to hydration reactions. If the green solution of TG is made alkaline, it is completely decolourized at a rate that is directly proportional to [OH⁻]. The above-mentioned reactions can be visualized with the following reaction scheme, which, however, does not consider the complications which arise in strongly acid solutions and which are discussed later in this paper. In the scheme is R = ⟨benzene ring⟩- N(CH₃)₂
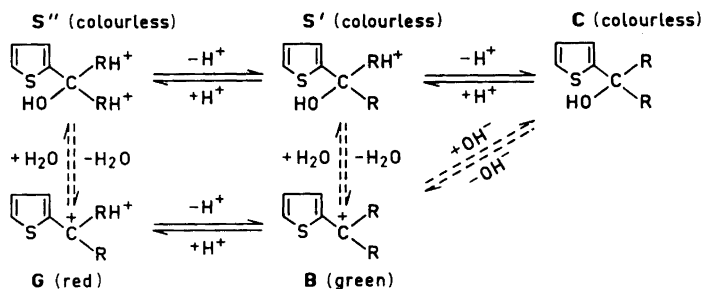
Full drawn arrows indicate that the reactions proceed at an immeasurable rate, *i.e.*, instantaneously, whereas dashed arrows indicate that the reactions take place at a measurable rate.

Definitions of constants and symbols

$$K_1 = \frac{[G]}{[B][H^+]} \ ; \ K_2 = \frac{[S'']_\infty}{[G]_\infty} \ ; \ K_3 = \frac{[S'][H^+]}{[S'']} \ ; \ K_4 = \frac{[C][H^+]}{[S']} \ ;$$

$$K_6 = \frac{[B]_\infty}{[S']_\infty}$$

h $= [H^+]$; oh $= [OH^-]$; $K_w = [H^+][OH^-]$.

$k_1 =$ rate constant for the reaction $\quad$ G + H₂O → S''

$k_2 =$ » $\quad$ » $\quad$ » $\quad$ » $\quad$ » $\quad$ S'' → G + H₂O

$k_3 =$ » $\quad$ » $\quad$ » $\quad$ » $\quad$ » $\quad$ B + H₂O → S'

$k_4 =$ » $\quad$ » $\quad$ » $\quad$ » $\quad$ » $\quad$ S' → B + H₂O

$k_5 =$ » $\quad$ » $\quad$ » $\quad$ » $\quad$ » $\quad$ B + OH⁻ → C

$k_6 =$ » $\quad$ » $\quad$ » $\quad$ » $\quad$ » $\quad$ C → B + OH⁻

$k =$ » $\quad$ » $\quad$ » $\quad$ » $\quad$ total reaction

ε_B, ε_G $\quad$ = the molar extinction coefficient of B and G

e_0, e_t, e_∞ = the absorbancy per cm of a solution at the times 0 and t and at equilibrium.

E_0, E_t, E_∞ = the total absorbancy.

e_B, e_G = the absorbancy per cm of a solution containing only B or G.

C_M = the total concentration of dyestuff.

The constants in the equilibrium scheme can be calculated, if the following quantities are determined for a large number of solutions with varying pH:

1. The absorbancy, e_0, at a moment immediately after the mixing of a dye stock solution with the appropriate buffers. The dye stock solution is (if possible) prepared in such a way that all of the dye is present as the coloured species B.
2. The absorbancy, e_∞, when equilibrium is reached.
3. The pH of the solutions.
4. The total rate constant, k, for the reactions that change the intensity of the colour of the solutions either by the hydration of the coloured species (B and G) to colourless species (C, S', S'') or vice versa.

Equations

The following equations are used for the calculations of the constants in the reaction scheme

$$e_0 = \frac{e_B + hK_1 e_G}{1 + hK_1} \tag{1}$$

$$e_\infty = \frac{e_B + hK_1 e_G}{1 + 1/K_6 + K_4/hK_6 + hK_1(1 + K_2)} \tag{2}$$

$$k = \frac{k_2 h^2 + k_4 hK_3 + k_6 K_3 K_4}{h^2 + hK_3 + K_3 K_4} + \frac{k_1 hK_1 + k_3 + k_5 oh}{1 + hK_1} \tag{3}$$

Eqn. (1) is transformed to

$$\frac{h}{e_B - e_0} = \frac{h}{e_B - e_G} + \frac{1}{K_1(e_B - e_G)} \tag{4}$$

and K_1 is determined by a graphical method.

In acid solutions, pH $\leq$ 2, we can approximate eqn. (2) and write

$$K_2 = \frac{e_G}{e_\infty} + \frac{e_B - e_\infty(1 + hK_1 + 1/K_6)}{hK_1 e_\infty} \tag{5}$$

In weakly alkaline solutions eqn. (2) is approximated and transformed to

$$\frac{h}{e_\infty} = h\frac{1 + K_6}{K_6 e_B} + \frac{K_4}{K_6 e_B} \tag{6}$$

According to eqn. (6), a straight line can be obtained, from which $(1 + K_6)/K_4$ is obtained.

EXPERIMENTAL

Chemicals and solutions. Thiophene Green. The leuco base was prepared according to
Levi [1] by the condensation of N,N-dimethylaniline with 2-thiophenealdehyde. We used
concentrated hydrochloric acid as a condensing agent, however, instead of zinc chloride.
The leuco base was recrystallized from ethanol and obtained as light brown needles
(m.p. 92—94°). The oxidation to dyestuff was performed with lead dioxide, added to a
cooled solution of the leuco base dissolved in dilute hydrochloric acid. After the addition
of sodium sulphate, lead sulphate and the remaining lead dioxide was filtered off.

The perchlorate of the dyestuff was precipitated with sodium perchlorate and was
recrystallized twice from 3 % and 0.1 % acetic acid, respectively. The perchlorate was
obtained as shining green needles with a violet lustre when viewed from certain angles.
(Found: C 57.9; H 5.42; N 6.29; Cl 8.18; S 7.5. Calc. for $C_{21}H_{23}O_4N_2ClS$: C 58.0; H 5.33;
N 6.44; Cl 8.15; S 7.37).

Stock solutions of the dye were prepared in the same manner as in Ref.[6] The chemicals
used for the buffers and the apparatus used for the measurements were the same as in Ref.[6]

MEASUREMENTS AND RESULTS

In acetate buffer, pH = 4.8 Thiophene Green produces only one coloured
species and more than 99 % of the dye is present as the coloured ion B. In
Fig. 1 there can be seen the absorption curves for the green ion B in acetate
buffer and for the red-yellow ion G in 0.2 M hydrochloric acid. The molecular
extinction coefficients were calculated from the experimentally obtained
absorption curves and eqn. (2) ($e_B = C_M \varepsilon_B$ and $e_G = C_M \varepsilon_G$). The following
values were obtained: $\lambda_{B\ max} = 628$ mμ and 467 mμ; $\varepsilon_{B\ max} = 7.5 \times 10^4$ and
2.55×10^4 resp. $\lambda_{G\ max} = 505$ mμ; $\varepsilon_{G\ max} = 2.80 \times 10^4$.

An absorption curve of TG in 98 % acetic acid and 2 % acetone gave
$\lambda_{B\ max} = 631$ mμ and 471 mμ; $\varepsilon_{B\ max} = 8.6 \times 10^4$ and 2.8×10^4, respectively.

Determination of K_1. The dye stock solution was mixed with an equivalent
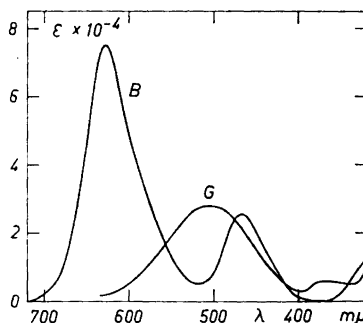volume of suitable HCl + KCl-buffers and e_0 was determined by extrapolation

Fig. 1. Thiophene Green. Absorption curves. B is the curve for the green ion
$[(Me_2NC_6H_4)_2CC_4H_3S]^+$ in acetate buffer, G is the curve for the yellow-red ion

$$\left[\begin{array}{c} Me_2NC_6H_4 \\ \diagdown \\ \diagup \\ Me_2HNC_6H_4 \end{array} CC_4H_3S \right]^{2+}$$ in dilute hydrochloric acid.
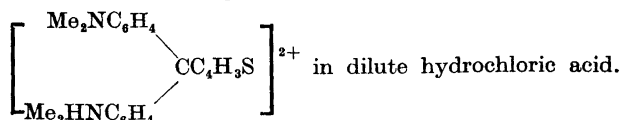
Table 1. Thiophene Green. e_0- and e_∞-values for the determination of K_1 and K_2. $\lambda = 630$ mμ, $C_M = 1 \times 10^{-5}$ M, $d = 1$ cm, $e_B = 0.720$, T $= 20.0°$C.

[H$^+$] M	e_0	e_∞	K_2
0.010	0.562	0.302	3.99
0.020	0.464	0.192	3.97
0.030	0.398	0.142	3.92
0.040	0.342	0.112	3.93
0.050	0.304	0.092	3.99
0.060	0.275	0.078	4.01
0.070	0.247	0.069	3.95
0.080	0.228	0.0615	3.95
Mean value			3.96

Table 2. Thiophene Green. e_∞-values for the determination of $K_4/(K_6 + 1)$. $C_M = 1 \times 10^{-5}$ M, $d = 1$ cm, $\lambda = 630$ mμ, $T = 20.0°$.

[H$^+$] $\times 10^7$M	e_∞	[H$^+$] $\times 10^7$ M	e_∞
1.948	0.640	0.512	0.470
1.547	0.622	0.338	0.403
1.257	0.598	0.240	0.340
0.954	0.570	0.182	0.290
0.741	0.530	0.0911	0.174

of the absorbancies to $t = 0$. The measurements were carried out at the wavelength $\lambda = 630$ mμ. In Fig. 2 [H$^+$]/($e_B - e_0$) is plotted against [H$^+$]. A straight line is obtained. The slope l and the intercept y on the ordinate-axis of this line and eqn. (4) give ($e_B = 0.720$): $y = 0.0504$ M; $l = 1.405$; **$K_1 = 27.9 \pm 0.5$ M^{-1}**.

Determination of K_2. The dye stock solution was mixed with HCl + KCl-buffers and the equilibrium absorbancies, e_∞, were measured in 1 cm absorption cells. K_2 was calculated from eqn. (5), where $K_1 = 27.9$ is known and $1/K_6 \ll 1$. $e_B = 0.720$; $e_G = 0.008$ at the used wavelength, 630 mμ. The results are recorded in Table 1. From this table the mean value **$K_2 = 3.96 \pm 0.10$** is obtained.

Determination of $K_4/(K_6 + 1)$. A dye stock solution was mixed with appropriate phosphate buffers, pH $= 6.7$—8.0, and the equilibrium absorbancies, e_∞, where read after 30 h. $C_M = 1 \times 10^{-5}$, $d = 1$ cm, $\lambda = 630$ mμ. In Fig. 3 [H$^+$]/e_∞ is plotted against [H$^+$]. A straight line is obtained, which gives $l = 1.367$; $y = 0.382 \times 10^{-7}$ M and from eqn. (6) $K_4/(K_6 + 1) = 2.79 \times 10^{-8}$ M is obtained.

Determination of K_3K_4. The following expression for the equilibrium absorbancy can be derived

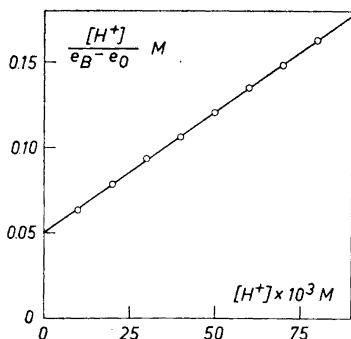$$e_\infty = \frac{e_B + K_1 h e_G}{1 + 1/K_6 + K_1 h + h/K_3K_6 + K_4/K_6 h} \tag{7}$$

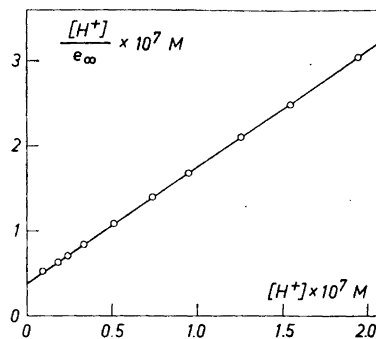*Fig. 2.* $[H^+]/(e_B - e_o)$ plotted against $[H^+]$ for the determination of K_1.

Fig. 3. $[H^+]/e_\infty$ plotted against $[H^+]$ for the determination of $K_4/(K_6 + 1)$.

In very weakly acid solutions, pH$>$3.5, K_1h can be neglected in the denominator and $K_1 h e_G$ in the numerator, if the measurements are carried out at a wavelength where $e_G \leq e_B$. After these approximations we can differentiate e_∞ in respect of $[H^+]$ and find that e_∞ has a maximum when $[H^+] = \sqrt{K_3 K_4}$. Fig. 4 is obtained by plotting e_∞ against $[H^+]$. From the figure $pH_{e_\infty max} = 4.79 \pm 0.01$ is obtained, which gives $\sqrt{K_3 K_4} = (1.62 \pm 0.04) \times 10^{-5}$ M. The accuracy of $K_3 K_4$ is not very high, since the curve is rather flat in a large pH-range on both sides of the maximum.

There is, however, another, more accurate method of determining $K_3 K_4$. We can write eqn. (3) as follows, since $hK_1 \lll 1$ in the actual pH-range,

$$\frac{k_4 h K_3}{h^2 + hK_3 + K_3 K_4} + k_3 = k - \frac{k_2 h^2 + k_6 K_3 K_4}{h^2 + hK_3 + K_3 K_4} - \frac{k_1 h K_1 + k_5 oh}{hK_1 + 1} = k - A \quad (8)$$

In eqn. (8) A is a correction term which amounts to 1—5 % of k in the pH-range 5.5—4.2. Therefore, it is not necessary to know the constants in the term A at any high degree of accuracy in the following treatment of eqn. (8). If eqn. (8) is differentiated with respect to $[H^+]$, it is found that $k - A$ has a maximum when $[H^+] = \sqrt{K_3 K_4}$

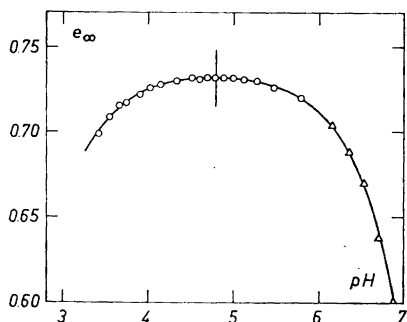$$(k - A)_{max} = \frac{k_4 K_3}{K_3 + 2\sqrt{K_3 K_4}} + k_3 \quad (9)$$

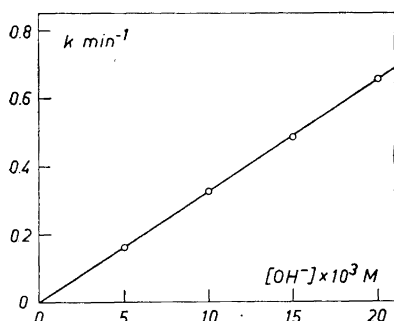*Fig. 4.* e_∞ as a function of pH for the determination of $K_3 K_4$.

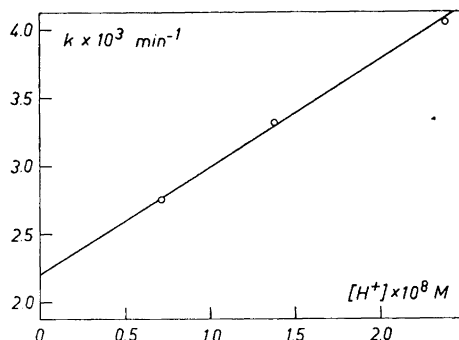*Fig. 5.* k plotted against [OH$^-$] for the determination of k_5.

Fig. 6. k plotted against [H$^+$] for the determination of k_3.

Through kinetic measurements, which are reported below, $k-A$ was found to have a maximum when pH $= 4.795 \pm 0.005$ giving $\sqrt{K_3 K_4} = (1.60 \pm 0.02) \times 10^{-5}$ M; $k_{max} = 0.274$ min^{-1} and $(k-A)_{max} = 0.271$ min^{-1}. The value of $\sqrt{K_3 K_4}$ obtained in this way agrees well with the value obtained from the equilibrium measurements.

Determination of k_5. For alkaline solutions eqn. (3) can be used in the following approximated form

$$k = k_3 + k_5 \text{oh} + k_6 \tag{10}$$

The dye stock solution was mixed with NaOH + KCl-buffers and the fading rate was determined. In Fig. 5 the rate constant of the decolourization, k in eqn. (10), is plotted against [OH$^-$]. A straight line is obtained which passes almost through the origin. Consequently, $k_3 + k_6 \ll k_5 \text{oh}$ in the pH-range used and only k_5 can be determined from Fig. 5, which gives **$k_5 = 32.7 \pm 0.3$ M^{-1} min^{-1}**.

Determination of k_3 and K_4/K_6. The rate constant k_3 was determined from kinetic measurements in phosphate buffers, pH $7-8$. Eqn. (3) was approximated to

$$k = k_4 \text{h}/K_4 + k_3 \tag{11}$$

since $k_3 \gg k_5 \text{oh} + k_6$ in this pH-range. In Fig. 6 k is plotted as a function of [H$^+$]. The straight line obtained gives **$k_3 = 0.00221 \pm 0.00003$ min^{-1}** and $k_4/K_4 = 7.85 \times 10^4$ min^{-1} M^{-1}. But since $k_4 = k_3 K_6$, we get $K_4/K_6 = 2.82 \times 10^{-8}$ M in excellent agreement with the value of $K_4/(K_6 + 1) = 2.79 \times 10^{-8}$ M, since $K_6 \gg 1$, obtained by equilibrium measurements which have been reported above.

Determination of K_3, K_4, K_6, k_4, and k_6. A dye stock solution was partially decolourized by making it 0.02 M with respect to hydrochloric acid. The following reactions then occur in the forward direction ($\rightarrow$): B + H$^+$ + H$_2$O $\rightleftarrows$ G + H$_2$O $\rightleftarrows$ S$''$ and B + H$^+$ + H$_2$O $\rightleftarrows$ S$'$ + H$^+$ $\rightleftarrows$ S$''$. This partially decolourized dye solution was then mixed with acetate buffers and the colour was more or
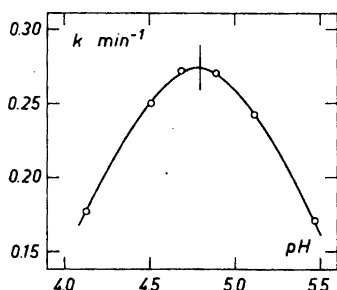
Fig. 7. The total rate constant k as a function of pH. The points represented by the symbols, O, are obtained experimentally. The curve is calculated from the non-approximated eqn. (3).
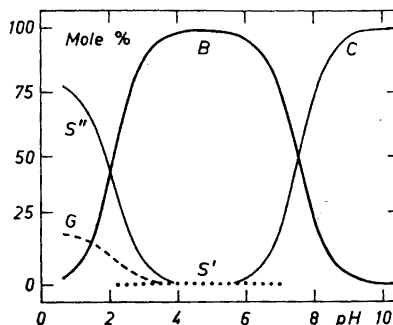

Fig. 8. The distribution of Thiophene Green between the different species as a function of pH.

less restored owing to the reactions above in the reverse direction. The rate constant for the restoring of the colour was determined at different pH-values.

In Fig. 7 k is plotted as a function of pH. Eqn. (9) can be written in the following form

$$(k-A)_{max} = \left(\frac{K_6}{K_4} \cdot \frac{K_3K_4}{K_3 + 2\sqrt{K_3K_4}} + 1 \right) k_3 \qquad (12$$

since $k_4 = k_3K_6$. From Fig. 7 $k_{max} = 0.274$ min^{-1} is obtained and $(k-A)_{max} = 0.271$ min^{-1} using approximate values of the constants in the correction term A. In eqn. (12) $K_3K_4 = 2.57 \times 10^{-10}$ M^2 is known (cf. p. 1843) and so is k_3 and K_6/K_4. Consequently, K_3 can be calculated. The following results were obtained $K_3 = (4.38 \pm 0 08) \times 10^{-5}$ M, $K_4 = (5.87 \pm 0.10) \times 10^{-6}$ M, $K_6 = 209 \pm 4$, $k_4 = 0.462 \pm 0.010$ min^{-1}. The rate constant $k_6 = (1.44 \pm 0.06) \times 10^{-5}$ min^{-1} is obtained from $k_6 = k_5K_WK_6/K_4$, $(K_W = 1.24 \times 10^{-14}$ M^2).

The distribution of Thiophene Green between the different species at equilibrium is calculated for different pH-values and shown as a function of pH in Fig. 8.

Table 3. Thiophene Green. The total rate constant, k, from kinetic measurements in HCl + KCl-buffers and the rate constant k_1 calculated from eqn. (13). $C_M = 1 \times 10^{-5}$ M, $d = 1$ cm, $\lambda = 630$ and 500 mμ, $T = 20.0°C$.

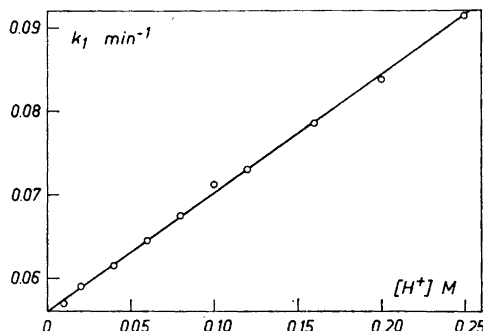| [H$^+$] M	k min^{-1}	k_1 min^{-1}	[H$^+$] M	k min^{-1}	k_1 min^{-1}
0.010	0.0307	0.0569	0.100	0.0712	0.0712
0.020	0.0385	0.0590	0.120	0.0753	0.0730
0.040	0.0495	0.0615	0.160	0.0845	0.0775
0.060	0.0578	0.0645	0.200	0.0928	0.0838
0.080	0.0647	0.0675	0.250	0.1036	0.0914

Fig. 9. The rate constant k_1 calculated from eqn. (13) plotted against [H⁺].

Determination of k_1 and k_2. These rate constants were determined by kinetic measurements of the decolourization, which is caused by the reactions G + $H_2O \rightleftharpoons$ S″ and B + $H_2O \rightleftharpoons$ S′, when a dye stock solution is mixed with HCl + KCl-buffers. Eqn. (3) can be approximated and since $k_2 = k_1/K_2$, it is transformed to

$$k_1 = \frac{k - k_4K_3/\mathrm{h} - k_3/(1 + K_1\mathrm{h})}{1/K_2 + K_1\mathrm{h}/(1 + K_1\mathrm{h})} \tag{13}$$

and k_1 can be calculated from eqn. (13) — K_1, K_2, k_3, and k_4 are known. Table 3 contains k-values experimentally found and values of k_1 calculated from eqn. (13). As can be seen from Table 3, k_1 is not constant but increases with [H⁺]. In Fig. 9 the values of k_1 are plotted against [H⁺]. A straight line is obtained and an extrapolation to [H⁺] = 0 gives **k_1 = 0.056 ± 0.0005 min⁻¹; k_2 = 0.0141 ± 0.0004 min⁻¹** since $k_2 = k_1/K_2$.

DISCUSSION

If the corresponding figures in Table 4 are compared, it is found that the reactions B + $H_2O \xrightarrow{k_3}$ S′ and G + $H_2O \xrightarrow{k_1}$ S″ are notably more slow in Thiophene Green than in Malachite Green. At the same time the values of the

Table 4. Comparison between corresponding constants of Malachite Green, *o*-hydroxy MG, *o*-methoxy MG, and Thiophene Green.

|	$1/K_1$	$K_3 \times 10^5$	$K_4 \times 10^6$	K_2	$1/K_6$	k_1 min⁻¹	k_2 min⁻¹	k_3 min⁻¹	k_4 min⁻¹
Malachite Green	0.036	2.7	5.8	22	0.0147	0.168	0.0078	0.00647	0.44
o-Hydroxy MG	0.034	3.30	4.2	3.93	0.0038	0.045	0.0114	0.00129	0.34
o-Methoxy MG	0.033	2.83	3.7	4.65	0.0040	0.050	0.0107	0.00177	0.45
Thiophene Green	0.036	4.38	5.9	3.96	0.0048	0.056	0.0141	0.00221	0.46

hydration constants K_2 and $1/K_6$ are lowered — that is, the equilibria are more displaced towards the coloured species in Thiophene Green than in Malachite Green. This depends on the thiophene sulphur, which increases the electron density on the central methane carbon and makes the addition of a polarized water molecule more difficult.

The exchange of a phenyl-group in MG for a thienyl-group has about the same effect as the substitution of an *ortho*-hydrogen in the phenyl-group for a hydroxy- or methoxy-group. See Table 4.

Thiophene Green and the hydroxy- and methoxy-derivatives of Malachite Green are similar in another respect too. Previous investigations show that the rate constant k_1 of p-hydroxy, p-methoxy (Ref. [4]), o-methoxy (Ref.[7]), and o-hydroxy Malachite Green [8] increases somewhat with [H$^+$], when k_1 is calculated from the reaction scheme on p. 1838. The value of k_1 of the *para*-derivatives increases with about 11 % in the range [H$^+$] = 30—100 mM, whereas the corresponding increase of the *ortho*-derivatives is about 6 % in the range [H$^+$] = 10—100 mM. In Thiophene Green k_1 increases with 60 % in the range [H$^+$] = 10—250 mM. This effect is not noticeable in the other investigated dyes.

The fact that k_1 increases linearly with [H$^+$] in some dyes makes it reasonable to believe that the reaction scheme, which has been used, does not cover all the reactions which influence the results of the measurements.

In strongly acid solutions the dye can probably bond another proton according to the following scheme, which only shows the reactions in strongly acid solutions.

(Scheme II)
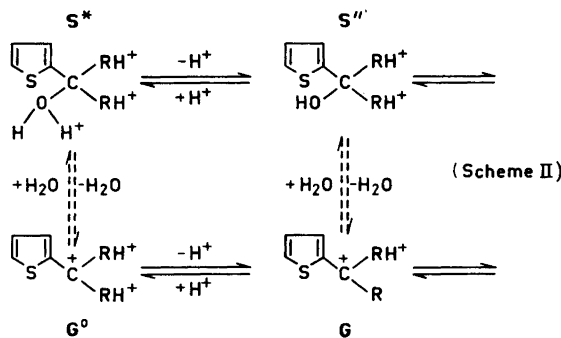
The following constants are defined

$$K_o = \frac{[G][H^+]}{[G^o]} ; \quad K'_o = \frac{[S''][H^+]}{[S^*]} ; \quad K = \frac{[S^*]_\infty}{[G^o]_\infty}$$

$k'_1 =$ rate constant for the reaction $G^o + H_2O \rightarrow S^*$

$k'_2 =$ »   »   »   »   » $S^* \rightarrow G^o + H_2O$

The fact that the determination of K_1 and K_2 is not obstructed by the presence of the species G^o and S^*, indicates that $[G^o]_o \ll [B]_o + [G]_o$ and $[S^*]_\infty \ll [B]_\infty + [G]_\infty + [S'']_\infty$ in the pH-range 1—2, where K_1 and K_2

are determined. However, the kinetics can be influenced by the presence of even very low concentrations of G° and S^*, if k_1' and k_2' are large compared with k_1 and k_2.

The following equations for the kinetics in solutions with pH < 7 can be derived, if the reaction scheme on p. 1846 is assumed to be valid

$$k = \frac{h^2 k_2' + h k_2 K_o' + k_4 K_o' K_3}{h^2 + h K_o' + K_o' K_3} + \frac{h^2 k_1' + h k_1 K_o + k_3 K_o K_1}{h^2 + h K_o + K_o/K_1} \qquad (14)$$

In the pH-range which has been used in Fig. 9, pH $= 0.6-2$, it holds that $h \gg K_3$ and $K_o' \gg h$, and eqn. (14) can, therefore, be approximated and at the same time rewritten as

$$k - k_4 K_3/h - k_3/(1 + K_1 h) = h k_2'/K_o' + k_2 + \frac{h k_1'/K_o + k_1}{1 + 1/K_1 h} \qquad (15)$$

$$= \frac{h k_1'/K_o + k_1}{K_2} + \frac{h k_1'/K_o + k_1}{1 + 1/K_1 h} \qquad (16)$$

since $k_1' = K k_2'$, $k_1 = K_2 k_2$, and $K_o' K = K_o K_2$. If we write $h k_1'/K_o + k_1 = k_1^\circ$ we finally get

$$k_1^\circ = \frac{k - k_4 K_3/h - k_3/(1 + K_1 h)}{1/K_2 + K_1 h/(1 + K_1 h)} \qquad (17)$$

The right member of eqn. (17) is identical with the right member of eqn. (13) and k_1° in eqn. (17) corresponds to k_1 in eqn. (13). If k_1° is plotted against $[H^+]$, a straight line should be obtained. Fig. 9 gives such a line with the intercept on the ordinate-axis $= k_1$ and the slope $= k_1'/K_o = 0.142$ min^{-1} M^{-1}.

Thus, the kinetic measurements strongly support the expanded reaction scheme. The individual values of the constants K_o, K, K_o', k_1', and k_2' cannot, however, be determined.

An attempt was made to determine the absorption curve of G° but the result was somewhat confusing. The absorption curves of Thiophene Green in various, strongly acidic solutions were recorded in the range $\lambda = 320 - 600$ mμ. A dye solution, which is made 5 M, 2.5 M, and 1 M with respect to HCl, contains at equilibrium about 90 %, 50 %, and 30 %, respectively, of the dye in the form of coloured species. The dye is not quite resistent to conc. HCl. An absorption curve obtained with the dye dissolved in 4.5 M H_2SO_4 was found to agree with Curve G (Fig. 1) within such narrow limits that only one of the curves has been drawn in Fig. 1. Curve G is calculated from eqn. (2) using the e_∞-values obtained from a solution with $[H^+] = 0.2$ M.

There are two possible explanations of the agreement between Curve G (Fig. 1) and the curve obtained in 4.5 M H_2SO_4. First: The species G° and G may have similar absorption curves in the used wavelength range. If this is true, the equilibrium $G^\circ + H_2O \rightleftharpoons S^*$ is strongly displaced towards the coloured G°. Second: The absorption curves of G° and G are not similar. If this is true, the ion G° does not reach measurable concentrations even in very strongly

acidic solutions. The marked increase of the colour of the dye, when the concentration of acid is raised, must then be explained as a very strong medium effect on the equilibrium $G + H_2O \rightleftharpoons S''$. We have found from other measurements of similar dyes that the equilibria "Coloured" $\rightleftharpoons$ "Colourless" are displaced towards the coloured species, if the dielectric constant of the solvent is decreased by the addition of organic substances such as ethanol, acetone and acetic acid, to an aqueous solution of the dye.

The reason for Thiophene Green, and probably p- and o-hydroxy and -methoxy Malachite Green too, reacting according to a more complicated scheme than that of MG and the rest of the investigated derivatives of MG, is the following: The thienyl-group as well as the hydroxy- and methoxy-substituted phenyl-group has a stronger electron donor character than the non-substituted phenyl-group. This is the reason why the reactions $S'' + H^+ \rightleftharpoons S^* \rightleftharpoons G^\circ + H_2O$ and $G + H^+ \rightleftharpoons G^\circ$ are so much facilitated that they manifest themselves in the kinetic measurements of Thiophene Green and the above-mentioned hydroxy- and methoxy-derivatives of MG. In Malachite Green and derivatives of MG with weakly electron-donating substituents these reactions may be possible, although they do not appreciably influence the kinetic measurements at pH $\approx$ 1.

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